UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

MIDTERM EXAMINATION

CHEMISTRY 351

Version

01

November 4th, 2021 Time: 2 Hours

READ THE INSTRUCTIONS CAREFULLY

PLEASE WRITE YOUR **NAME**, **STUDENT I.D. NUMBER** ON ***BOTH*** **YOUR ANSWER BOOKLET** AND **COMPUTER ANSWER SHEET**.

ENTER **VERSION NUMBER 01** ON THE **COMPUTER ANSWER SHEET**

The examination consists of Parts 1 - 7, each of which should be attempted. Note that some parts provide you with a choice of questions, *e.g*. answer 4 out of 5. These will be graded in numerical order until the required number have been graded, regardless of whether they are right or wrong. Parts 1 - 4 will be computer graded, and only Parts 5, 6, and 7 are to be answered in the blue booklet provided.

Parts 1 - 4 consist of a series of multiple choice questions numbered 1 - 31 which are to be answered on your computer answer sheet (no extra time is provided for "bubbling" in the score sheet). Indicate your answer by blackening out the appropriate space, A, B, C, D or E on the answer sheet. Use a ***pencil only*** and ***not ink***. In some cases it is required that you indicate ***multiple*** items for a complete and/or correct answer by blackening out more than one space. In some other cases more than five options are available and some of these also require more than one space to be blackened out. For an example, an option specified as AB requires that you blacken out ***both*** space A and space B. Part marks may be awarded in some of the questions. Incorrect answers must be erased ***cleanly***.

A periodic table with atomic numbers and atomic weights and infrared data tables are located on the last two pages

Molecular models are permitted during the exam; calculators are also permitted, ***but NOT programmable calculators***. **Absolutely no other electronic devices are allowed.**

14% PART 1: RELATIVE PROPERTIES

ANSWER ANY SEVEN (7) of questions 1-8 (2 marks per question)

Arrange the items in questions 1-8 in DECREASING ORDER (*i.e.* greatest, most etc. first) with respect to the indicated property.

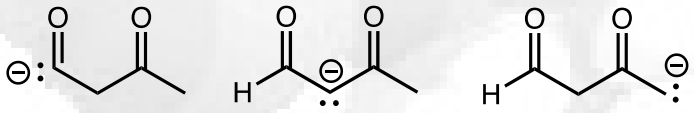
Use the following code to indicate your answers.

A.	**i > ii > iii**	**D.**	**ii > iii > i**
B.	**i > iii > ii**	**E.**	**iii > i > ii**
C.	**ii > i > iii**	**AB.**	**iii > ii > i**

1. The formal charge on each of the bolded atoms shown below (all lone pairs are shown):

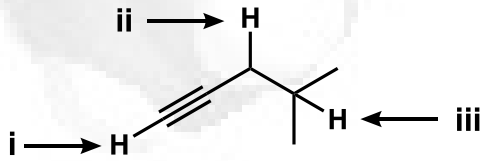
i **ii** **iii**

2. The relative stabilities of the following carbanions:

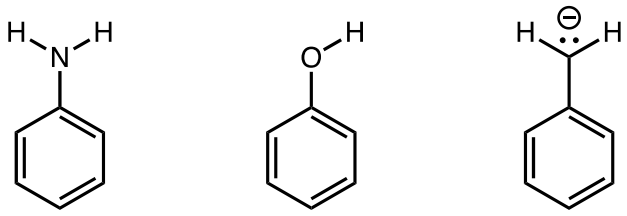


i **ii** **iii**

3. The strengths of the **C-H** bonds indicated below:



4. The relative basicity of each of the following:

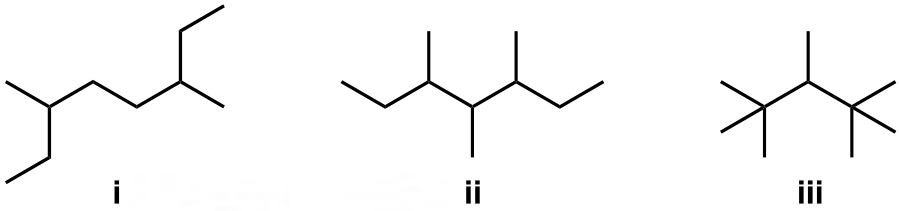


i **ii** **iii**

Use the following code to indicate your answers.

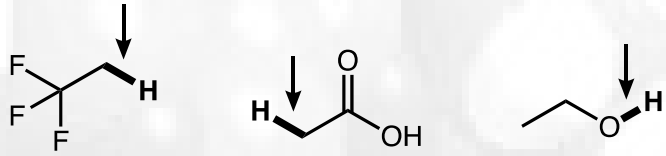
A.	**i > ii > iii**	**D.**	**ii > iii > i**
B.	**i > iii > ii**	**E.**	**iii > i > ii**
C.	**ii > i > iii**	**AB.**	**iii > ii > i**

5. The relative stability of the following isomers:



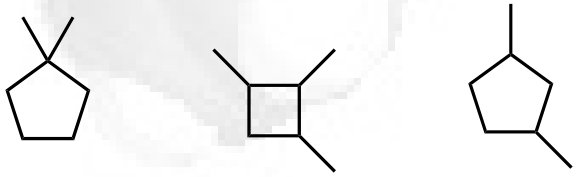
i **ii** **iii**

6. The relative acidity of the indicated bonds to hydrogen:



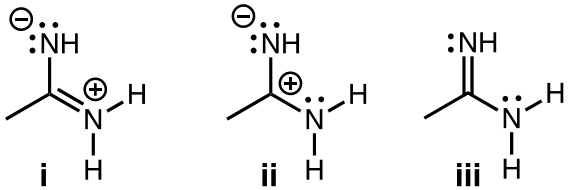
i **ii** **iii**

7. The number of different monochlorinated constitutional isomers formed by the reaction of each of the following molecules with chlorine in the presence of uv light.



i **ii** **iii**

8. The relative importance of the following resonance structure of the “amidine” functional group.



i **ii** **iii**

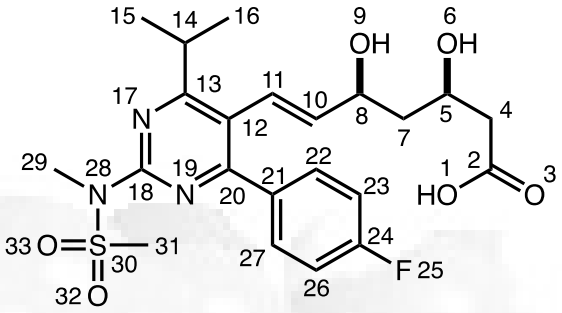
18% **PART 2: MOLECULAR PROPERTIES**

ANSWER ALL of the questions 9 – 17

For each of the questions 9 - 17 select the appropriate answer(s) from the answers provided. In some cases more than one selection may be required for full credit.

Questions 9-17 all refer to Crestor, cholesterol modifying statin drug (structure shown below):

Crestor



9. Which atom is the most acidic hydrogen bonded to ?

A. C4 **B.** C31 **C.** O1 **D.** O6 **E.** O9

10. What type of orbital does the lone pair of **N17** occupy ?

A. sp **B.** sp^2 **C.** s **D.** sp^3 **E.** p

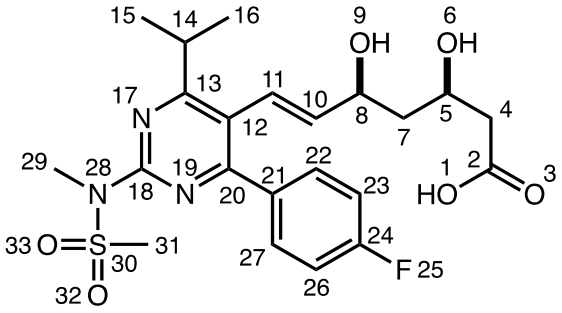
11. What are the hybridisations of **O1** and **O6** respectively ?

A. sp^2, sp^2 **B.** sp^3, sp^2 **C.** sp^3, sp^3 **D.** sp, sp^2 **E.** sp^2, sp^3

12. Which of the following functional groups are found in Crestor ?

A. ester **B.** ether **C.** alcohol **D.** phenol **E.** alkene

Crestor



13. What is the oxidation state of **C24?**

A. –2 **B.** –1 **C.** 0 **D.** +1 **E.** +2

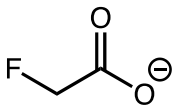
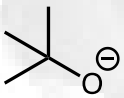
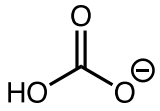
14. Which of the following bonds is the shortest?

A. C13-N17 **B. N19-C20** **C. C20-C21** **D. C10-C11** **E. N28-S30**

15. Which of the following atoms is the most basic?

A. N17 **B.** F25 **C.** C14 **D.** O6 **E.** O1

16. If Crestor were reacted with TWO equivalents of each of the bases listed below, which base would fully (>98%) deprotonate O1, but would not significantly (<2%) deprotonate O9?

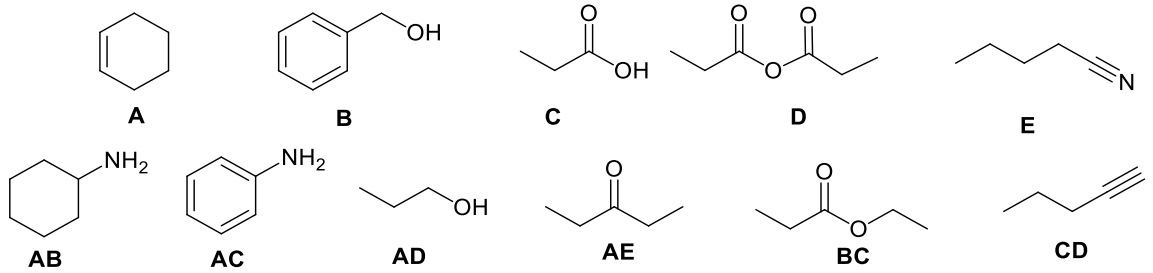
A.  **B.**  **C.**  **D.**  **E.** 

17. Which term best describes **C16** ?

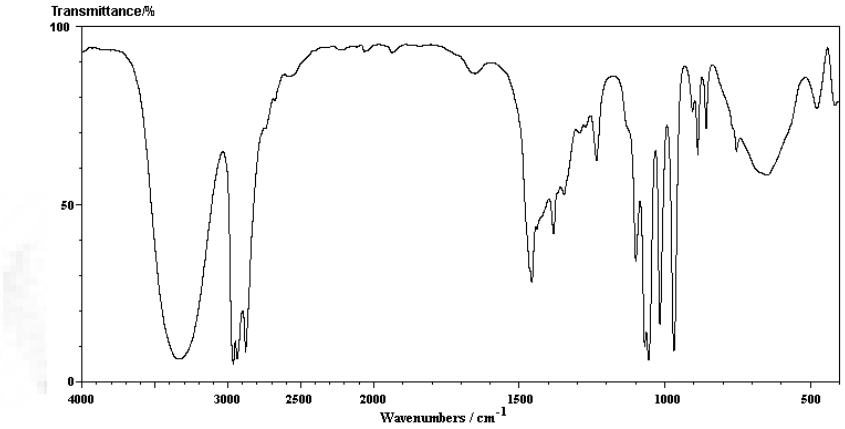
A. primary **B.** secondary **C.** tertiary **D.** benzylic **E.** allylic

15% **PART 3: SPECTROSCOPY**

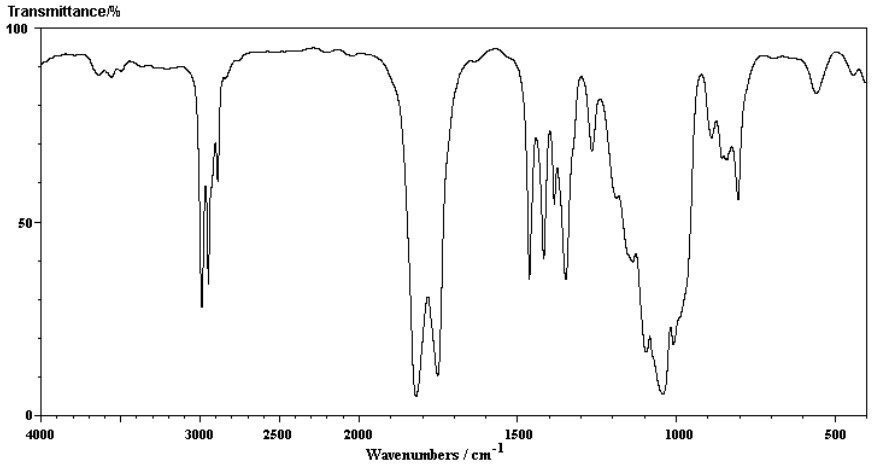
For each of the questions 18-23, match the IR spectra to a structure in the list below:



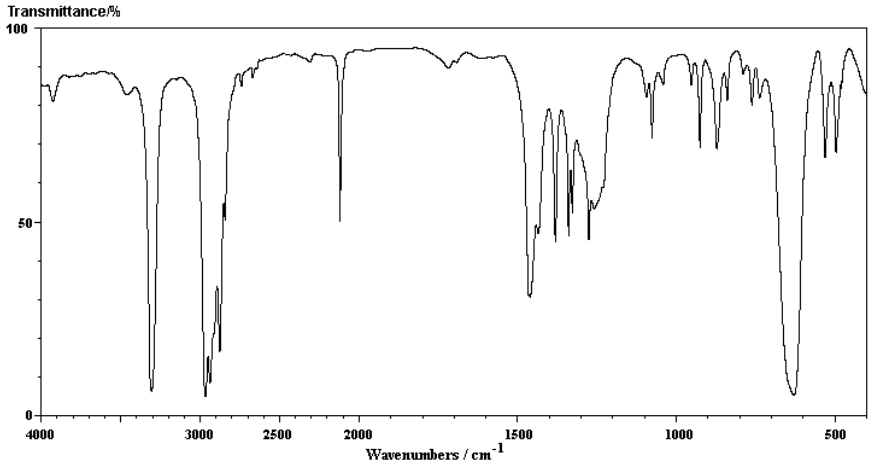
18.

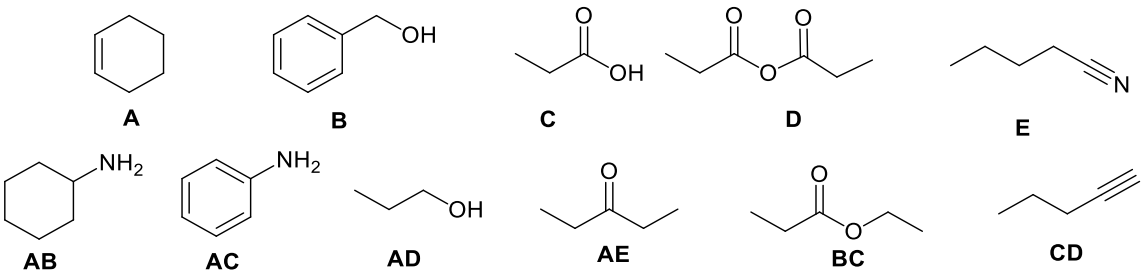


19.

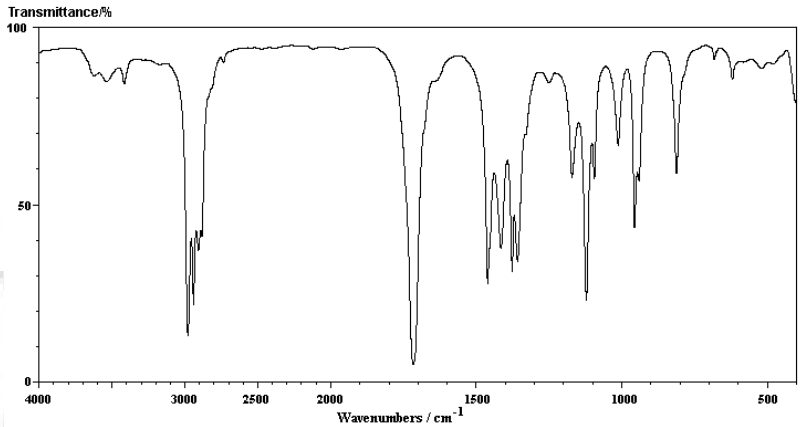


20.

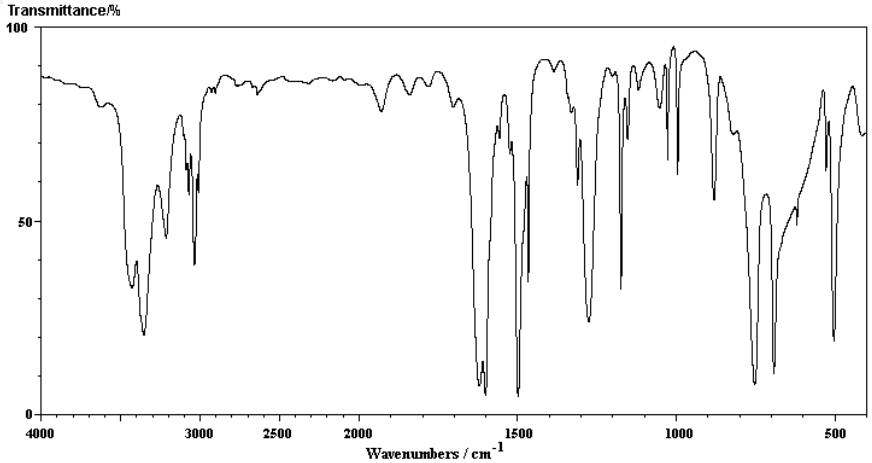



A
B
C
D
E
AB
AC
AD
AE
BC
CD

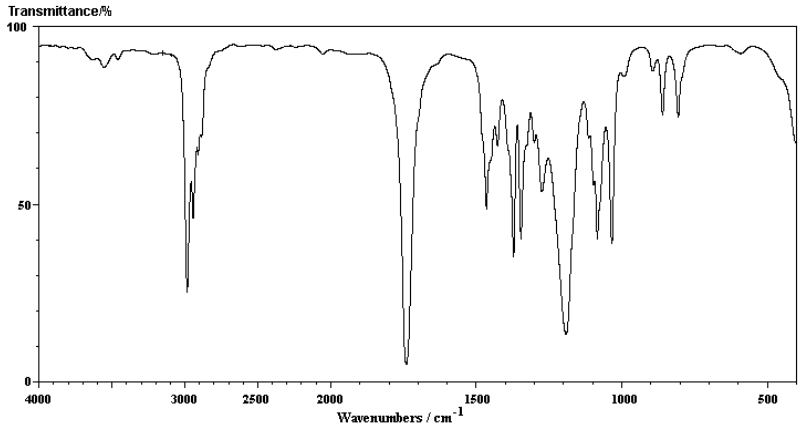
21.


Transmittance/%
100
50
0
4000
3000
2500
2000
1500
1000
500
Wavenumbers / cm-1

22.


Transmittance/%
100
50
0
4000
3000
2500
2000
1500
1000
500
Wavenumbers / cm-1

23.

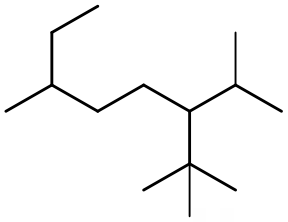

Transmittance/%
100
50
0
4000
3000
2500
2000
1500
1000
500
Wavenumbers / cm-1

14% **PART 4: NOMENCLATURE**

ANSWER ANY SEVEN (7) of the questions 24-31 (2 marks per question).

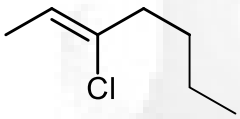
For each of questions 24 to 27, select the correct IUPAC name for the compound shown:

24.



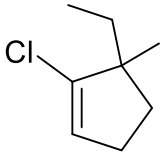
A. 3-tert-butyl-2,6-dimethyloctane
B. 2,6-dimethyl-3-tert-butyloctane
C. 3-tert-butyl-6-ethyl-2-methylheptane
D. 2,2,6-trimethyl-3-propyloctane
E. 3-(1-methylethyl)-2,2,6-trimethyloctane
AB.2,2,6-trimethyl-3-(1-methylethyl)octane

25.



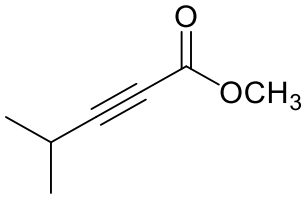
A. *cis*-1-methyl-2-chlorohex-1-ene
B. *trans*-1-methyl-2-chlorohex-1-ene
C. *cis* -3-chlorohept-2-ene
D. *trans*-3-chlorohept-2-ene
E. *cis* -2-chloro-1-methylhex-2-ene
AB. *trans*-2-chloro-1-methylhex-2-ene

26.



A. 3-ethyl-3-methyl-2-chlorocyclopentene
B. 1-chloro-5-ethyl-5-methylcyclopentene
C. 2-chloro-3-ethyl-3-methylcyclopentene
D. 1-chloro-2-ethyl-2-methylcyclopentene
E. 1-ethyl-1-methyl-2-chlorocyclopentene
AB 1-chloro-5-ethylmethylcyclopentene

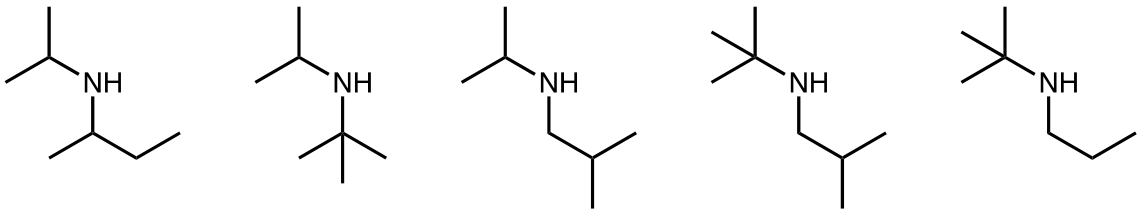
27.



A. methoxy 4-methylpent-2-ynal
B. methyl 4-methylpent-ynone
C. 1,4-dimethylpent-2-ynone
D. methyl 3-isopropylprop-ynoate
E. 4-methyl-1-methoxypent-2-ynoate
AB. methyl 4-methylpent-2-ynoate

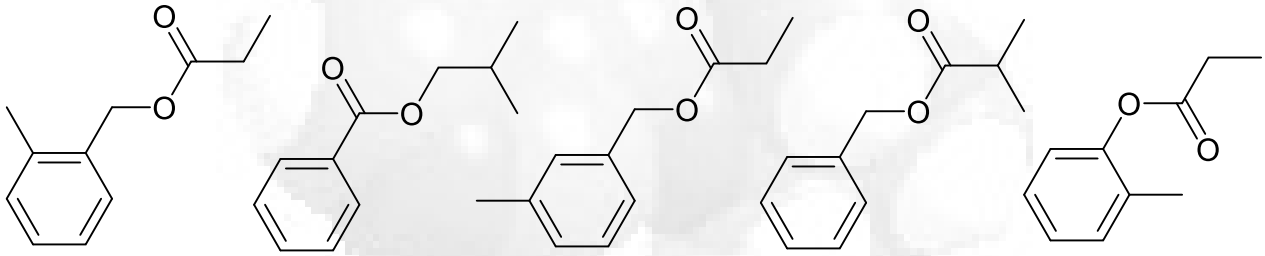
For each of questions 28 to 31, select the correct structure for the IUPAC name provided:

28. N-isopropyl-tert-butylamine



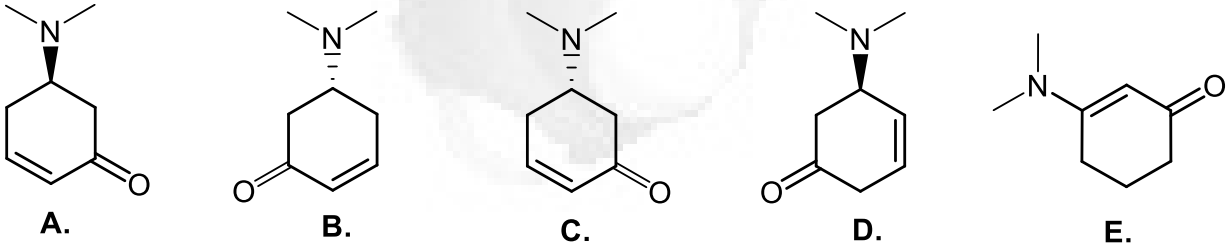
A. **B.** **C.** **D.** **E.**

29. 2-methylbenzyl propanoate



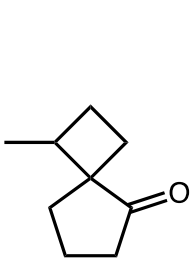
A **B** **C** **D** **E**

30. (S)-5-(N,N-dimethylamino)cyclohex-2-en-1-one

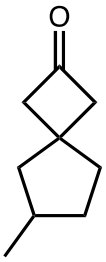


A. **B.** **C.** **D.** **E.**

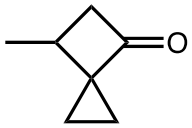
31. 6-methylspiro[3.4]octan-2-one:



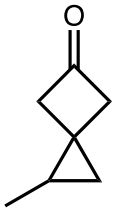
A.



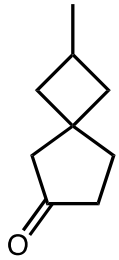
B.



C.



D.



E.

13% **PART 5: STRUCTURE DETERMINATION**

Write your answer in the booklet provided. For FULL marks you MUST show your work. PARTIAL marks will be awarded.

Each of the following questions needs to be answered based on compound **X** which has the molecular formula $C_8H_8O_2$.

a) What is the molecular weight of compound **X** ?

b) What is the index of hydrogen deficiency of compound **X**?

c) Draw a structure for **X** that would be soluble in 5% $NaHCO_3$ solution.

d) Draw a structure for **X** that would have a broad IR peak at 3300 cm^{-1}, would be soluble in NaOH solution (but ***not*** $NaHCO_3$), and contains six types of carbon, and four types of hydrogen.

e) Draw a structure for **X** where the most acidic proton has a pKa >20

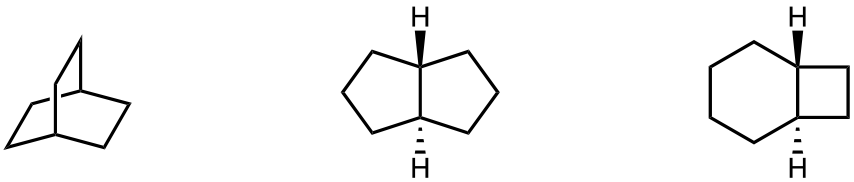
f) Draw a structure for **X** that has no significant IR peaks between 1685–1800 cm^{-1}

g) Name 3 oxygen containing functional groups that could be present in isomers of **X**

13% **PART 6: THERMODYNAMICS**

Write your answer in the booklet provided. For FULL marks you MUST show your working. PARTIAL marks will be awarded.

Three isomers of C_8H_{14} are shown below:



i **ii** **iii**

a) Write a balanced reaction equation for the complete combustion of isomer **i**.

b) Calculate $\Delta H_f°$ of isomer **iii**, given that the following heats of combustion:

$\Delta H_C°$,C (graphite) = -94.1 kcal/mol

$\Delta H_C°$,H_2 (gas) = -68.3 kcal/mol

$\Delta H_C°$,isomer iii = -1214.3 kcal/mol

c) Given that the heat of formation, $\Delta H_f°$ of isomer **i** is -35.4 kcal/mol and that of isomer **ii** is -26.4 kcal/mol: calculate the corresponding $\Delta H_C°$ values for each.

d) Draw an energy diagram to illustrate the relative energy difference between all three isomers **i**-**iii**, with clearly labeled reactants, products, and all $\Delta H_f°$ and $\Delta H_C°$ values, and indicate which one is the most stable isomer and which one is the lease stable.

e) Only ***one*** of these molecules is chiral. Which one is it? Why are the other two molecules not chiral?

f) Draw another isomer of C_8H_{14} that has a bicyclo[2.2.1] structure.

13% **PART 7: MECHANISM**

Write your answer in the booklet provided. For FULL marks you MUST show your working. PARTIAL marks will be awarded.

a) Draw a mechanistic sequence using double headed (*i.e.* electron pair) curly arrows that represents the reaction sequence described verbally by the following points in which (*E*)-4-methyl-4-hexene-1-ol cyclizes in the presence of a catalytic amount of hydrochloric acid.

Step 1. Reaction of the pi-electrons of the alkene with hydrochloric acid to generate a tertiary carbocation and a chloride ion.

Step 2. Attack of the alcohol functional group as a nucleophile on the carbocation to generate an oxonium ion.

Step 3. Removal of the most acidic hydrogen atom in the molecule by chloride ion to regenerate the hydrochloric acid catalyst and yield the final product.

b) This reaction generates a new chiral center. Draw one enantiomer of the product using wedge/hash notation. Clearly label the priority of the 4 groups on the chiral center, and assign the chiral center you have drawn as (*R*) or (S*)*.

c) If you did this reaction with the (*Z*) isomer of the starting material instead, do you think you would make the same product? Justify your answer.

**** THE END ****

IRH / CCL / JVH F2021

INFRA-RED GROUP ABSORPTION FREQUENCIES

		TYPE OF VIBRATION	FREQUENCY (cm^{-1})	WAVELENGTH (μ)	INTENSITY (1)
C–H	Alkanes	(stretch)	3000-2850	3.33-3.51	s
$-CH_3$		(bend)	1450 and 1375	6.90 and 7.27	m
$-CH_2-$		(bend)	1465	6.83	m
	Alkenes	(stretch)	3100-3000	3.23-3.33	m
		(bend)	1700-1000	5.88-10.0	s
	Aromatics	(stretch)	3150-3050	3.17-3.28	s
		(out-of-plane bend)	1000-700	10.0-14.3	s
	Alkyne	(stretch)	ca. 3300	ca.3.03	s
	Aldehyde		2900-2800	3.45-3.57	w
			2800-2700	3.57-3.70	w
C–C	Alkane	not usually useful			
C=C	Alkene		1680-1600	5.95-6.25	m-w
	Aromatic		1600-1400	6.25-7.14	m-w
C≡C	Alkyne		2250-2100	4.44-4.76	m-w
C=O	Aldehyde		1740-1720	5.75-5.81	s
	Ketone		1725-1705	5.80-5.87	s
	Carboxylic acid		1725-1700	5.80-5.88	s
	Ester		1750-1730	5.71-5.78	s
	Amide		1700-1640	5.88-6.10	s
	Anhydride		ca. 1810	ca. 5.52	s
			ca. 1760	ca. 5.68	s
	Acyl chloride		1800	5.55	s
C–O	Alcohols, Ethers, Esters,				
	Carboxylic acids		1300-1000	7.69-10.0	s
O–H	Alcohols, Phenols				
	Free		3650-3600	2.74-2.78	m
	H-Bonded		3400-3200	2.94-3.12	m
	Carboxylic acids (2)		3300-2500	3.03-4.00	m
N–H	Primary and secondary amines		ca. 3500	ca. 2.86	m
C≡N	Nitriles		2260-2240	4.42-4.46	m
N=O	Nitro ($R-NO_2$)		1600-1500	6.25-6.67	s
			1400-1300	7.14-7.69	s
C–X	Fluoride		1400-1000	7.14-10.0	s
	Chloride		800-600	12.5-16.7	s
	Bromide, Iodide		<600	>16.7	s

(1) s = strong, m = medium and w = weak

(2) note that the -OH absorption of solid carboxylic acids which run as a nujol mull can be difficult to see as they maybe very broad

Cont'd

PERIODIC TABLE

1 1A																	18 8A
1 **H** 1.008	**2** 2A											**13** 3A	**14** 4A	**15** 5A	**16** 6A	**17** 7A	2 **He** 4.003
3 **Li** 6.941	4 **Be** 9.012											5 **B** 10.81	6 **C** 12.01	7 **N** 14.01	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.18
11 **Na** 22.99	12 **Mg** 24.31	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.07	17 **Cl** 35.45	18 **Ar** 39.95
19 **K** 39.10	20 **Ca** 40.08	21 **Sc** 44.96	22 **Ti** 47.88	23 **V** 50.94	24 **Cr** 52.00	25 **Mn** 54.94	26 **Fe** 55.85	27 **Co** 58.93	28 **Ni** 58.69	29 **Cu** 63.55	30 **Zn** 65.38	31 **Ga** 69.72	32 **Ge** 72.59	33 **As** 74.92	34 **Se** 78.96	35 **Br** 79.90	36 **Kr** 83.80
37 **Rb** 85.47	38 **Sr** 87.62	39 **Y** 88.91	40 **Zr** 91.22	41 **Nb** 92.91	42 **Mo** 95.94	43 **Tc** (98)	44 **Ru** 101.1	45 **Rh** 102.9	46 **Pd** 106.4	47 **Ag** 107.9	48 **Cd** 112.4	49 **In** 114.8	50 **Sn** 118.7	51 **Sb** 121.8	52 **Te** 127.6	53 **I** 126.9	54 **Xe** 131.3
55 **Cs** 132.9	56 **Ba** 137.3	57* **La** 138.9	72 **Hf** 178.5	73 **Ta** 180.9	74 **W** 183.9	75 **Re** 186.2	76 **Os** 190.2	77 **Ir** 192.2	78 **Pt** 195.1	79 **Au** 197.0	80 **Hg** 200.6	81 **Tl** 204.4	82 **Pb** 207.2	83 **Bi** 209.0	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
87 **Fr** (223)	88 **Ra** 226.0	89** **Ac** (227)	104 **Rf** (261)	105 **Ha** (262)	106 **Sg** (263)	107 **Ns** (262)	108 **Hs** (265)	109 **Mt** (266)	110 **Uun** (269)	111 **Uuu** (272)							

Lanthanides *	58 **Ce** 140.1	59 **Pr** 140.9	60 **Nd** 144.2	61 **Pm** (145)	62 **Sm** 150.4	63 **Eu** 152.0	64 **Gd** 157.3	65 **Tb** 158.9	66 **Dy** 162.5	67 **Ho** 164.9	68 **Er** 167.3	69 **Tm** 168.9	70 **Yb** 173.0	71 **Lu** 175.0
Actinides **	90 **Th** 232.0	91 **Pa** 231.0	92 **U** 238.0	93 **Np** 237.0	94 **Pu** (244)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (260)